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Nitric acid in the stratosphere based on Odin observations from 2001 to 2007 – Part 2: High-altitude polar enhancements

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Abstract

The wintertime abundance of nitric acid (HNO_3) in the polar upper stratosphere displays a strong inter-annual variability, and is known to be strongly influenced by energetic particle precipitation, primarily during solar proton events, but also by precipitating electrons in the auroral zone. While wintertime HNO_3 enhancements in the polar upper stratosphere had been occasionally observed before, from the ground or from satellite, we present here measurements by the Sub-Millimeter Radiometer instrument aboard the Odin satellite through 6 full annual cycles (2001 to 2007). Major solar proton events, e.g. during November 2001 or the Halloween solar storms of autumn 2003, lead to a two-stage HNO_3 enhancement, likely involving different chemical reactions: a fast (about 1 week) in-situ enhancement from the mid to the upper stratosphere is followed by a slower, longer-lasting one, whereby anomalies originating in the upper stratosphere can descend within the polar vortex into the lower stratosphere. We highlight the fact that the actual chemical coupling between the upper and lower atmosphere involves a complex interplay of chemistry, dynamics and energetic particle precipitation.

1 Introduction

Nitric acid (HNO_3) is a key minor constituent of the middle atmosphere, part of the odd nitrogen family (NO_y), and a reservoir for the active nitrogen species (NO_x), which provide a major ozone loss catalytic cycle in the middle and upper stratosphere. In the lower stratosphere, HNO_3 plays a multi-facetted role in ozone depletion.

Stratospheric HNO_3 is produced through gas phase reaction of hydroxyl (OH) with NO_2, and heterogeneous chemical conversion of N_2O_5, the latter constituent being produced by gas phase reactions in the cold polar night conditions and easily thermally decomposed. The HNO_3 sinks are photo-dissociation and reaction with OH. Its photo-dissociation timescale is on the order of days in mid-latitudes. In the lower and middle stratosphere, HNO_3 has hence a pronounced seasonal cycle in the polar regions. The HNO_3-rich layer peaks at around 25–30 km at high latitudes in winter. Another sink of HNO_3 is the sequestration from the gas phase during polar stratospheric cloud formation, and its irreversible removal through sedimentation (denitrification).

Stratospheric HNO_3 has been observed by means of ground-based, balloon and aircraft and satellite instrumentation. The most complete dataset to date has been provided by the Microwave Limb Sounder (MLS) instrument aboard UARS (Santee et al., 2004), albeit not in the upper stratosphere. While the first part of this article (Urban et al., 2008) shows 6 annual cycles (2001–2007) of satellite observations of stratospheric HNO_3 by the "Odin Sub-Millimetre Radiometer" (SMR), we focus in this second part on describing the high-altitude polar enhancements, which have not been documented over so many years by other satellite instruments. In winter, enhanced layers of HNO_3 are commonly observed at high altitudes in the polar regions, as revealed by ground-based (de Zafra and Smyshlaev, 2001) or satellite observations (Austin et al., 1986; Lopez-Puertas et al., 2005b, hereafter LP05; Orsolini et al., 2005, hereafter OR05). These enhanced layers appear first in the uppermost stratosphere and tend to descend within the winter polar vortex. While recurrent, these enhancements vary widely in amplitude from year to year. Exceptionally strong enhancements have been linked to energetic particle precipitation (EPP) events and anomalous descent of mesospheric air.

Stratospheric NO_x abundances are amplified in-situ during the strongest solar proton events (SPEs) (also known as the NO_x direct effect), or through downward transport of mesospheric air (also known as the NO_x indirect effect), enriched in NO_x by EPP, i.e. SPEs or low energy electron precipitation from auroral activity. Various EPP events have led to upper-stratospheric NO_2 abundances over a hundred ppb (Callis and Lambeth, 1998; OR05; LP05). The best studied EPP case occurred during the violent "Halloween" solar storms and SPE of autumn 2003, when several satellite instruments observed not only HNO_3, but also a whole suite of complementary trace species, some for the first time within the polar night. The Michelson Interferometer for Passive Atmo-

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spheric Sounding (MIPAS) observations in particular, revealed a two-stage evolution of HNO_3 enhancements (LP05; OR05). Immediately following the SPE, a short-lived (about 1 week) stratospheric layer of enhanced HNO_3, peaking at 2–2.5 ppb, was observed above 35 km by LP05, who suggested formation through gas phase reactions with the enhanced OH abundance, and through ion chemistry in darkness. Newly reprocessed MIPAS retrievals indicate that the HNO_3 enhancements extend into the upper stratosphere and lower mesosphere (Lopez-Puertas, 2007). A weaker short-lived increase in HNO_3 was also observed in the southern hemisphere. Incidently, these short-lived chemical perturbations were not limited to NO_2 and HNO_3. MIPAS observed perturbed chlorine family species (ClO, HOCl) (von Clarmann et al., 2005), and O_3 depletion was observed by a variety of satellite instruments and confirmed by model studies (Lopez-Puertas et al., 2005a; Seppalla et al., 2004; Rohen et al., 2005; Jackman et al., 2005, 2007).

In a second stage, several weeks after the SPE, an anomalous HNO_3-rich layer was first observed at about 45 km (OR05), and intensified considerably while descending confined in vortex air. By mid-January, it has reached 30 km and vortex-averaged HNO_3 abundances were as high as 13–15 ppb, leading to double-peaked high-latitude HNO_3 profiles. Several mechanisms have been proposed to explain these long-lasting high-altitude HNO_3 enhancements, which invoke heterogeneous reactions converting N_2O_5 into HNO_3. de Zafra and Smyshlaev (2001) followed earlier suggestions (Bohringer et al., 1993) that hydrated ion clusters might be the seat of such heterogeneous reactions, albeit sulphate aerosols were suggested to play a role below 35 km (Bekki et al., 1995). This second stage requires a large downward flux of NO_2 to generate N_2O_5, but also a high degree of vortex confinement. The background abundance of hydrated ion cluster is thought to be generated by galactic cosmic rays.

One might call the first stage of HNO_3 enhancements, the fast effect, and the second stage the delayed effect. While the HNO_3 enhancements share some characteristics of the NO_x enhancements, such as high-altitude origin, polar confinement and descent, they do not need to follow or coincide with them. Late winter or spring NO_x pulses, like those observed in February–March 2004 and 2006 (Randall et al., 2005, 2006), might not give rise to HNO_3 enhancements, as the slow ion cluster chemistry requires a stable vortex, and coldness and darkness to build up HNO_3, conditions which are not provided close to the stratospheric final warming. These NO_x pulses nevertheless were important for the upper stratospheric ozone budget, leading for example to nearly 60% ozone destruction at 45 km in spring 2004 (Natarajan et al., 2004; Randall et al., 2005).

The aim of this paper is to show high-altitude HNO_3 polar enhancements, including the occasional two-stage time-development, in 6 annual cycles of Odin/SMR satellite observations from 2001 to 2007. The companion paper describes the characteristics of the satellite retrievals, and the climatology and variability in the lower stratosphere (Urban et al., 2008, cited above), neither of which are repeated here. The SMR HNO_3 observations allow revisiting some EPP events outside of the July 2002–March 2004 period studied by MIPAS (Stiller et al., 2003; LP05; OR05). Since July 2004, MLS aboard AURA makes also global observations of HNO_3 that cover the mid and upper stratosphere (Santee et al., 2007).

2 Polar HNO_3 enhancements from 2001 to 2007

Figure 1 shows at 1400 K, or approximately 40 km, the time evolution of HNO_3 as a function of equivalent latitude, revealing a series of 6 winter enhancements in both polar regions, with considerable inter-annual variability. The figure can be examined together with Figs. 2 and 3 in Urban et al. (2008), which show the descent of the anomalies from the upper stratosphere. Enhancements appear recurrently in winter as air with background NO_x levels descending from the mesosphere always provide some amount of NO_x and HNO_3 conversion (de Zafra and Smyshlaev, 2001), but with strong inter-annual variability. The SMR observations during 2001–2007 took place during the declining phase of the solar cycle, and a period with intense SPEs (Jackman et al., 2007). The largest enhancements in the NH follow the very strong SPE of November 2001, the SPEs of October–November 2003 (Halloween storms), and other SPEs in mid-January 2005 and mid-December 2006. In the SH, the largest enhancement occurred in austral winter 2003.

Next, we examine each individual winter in each hemisphere in Figs. 2 and 3, as time versus potential temperature cross-sections of polar cap averaged (equivalent latitudes poleward of 70° N) HNO_3. Both retrieved mixing ratios and anomalies from the winter average at each level are shown. Occurrences of SPE and major (class X) SPE events are shown by pink circles (open and full circles with connecting lines, respectively). For brevity, we only discuss the strongest enhancements.

2.1 Northern Hemisphere

Winter 2001/2002. We see clear evidence for a two-stage development, with a short-lived layer enriched in HNO_3, following the November 2001 SPE, above 1200 K and extending upward into the upper stratosphere-lower mesosphere. Later, the descending layer enriched in HNO_3 shows the strongest and longer-lasting anomalies from the SMR record in the NH.

Winter 2002/2003. No SPE occurred during that winter, which witnessed only a weak polar enhancement.

Winter 2003/2004. The two-stage development first seen in MIPAS (LP05; Lopez-Puertas, 2007; OR05) is confirmed by the SMR data. During the first stage (fast effect), which extends from above 1300 K into the upper stratosphere-lower mesosphere, the mixing ratios anomalies are smaller than the 2–2.5 ppb in MIPAS data (near 45 km), but are reduced due to time smoothing applied here. In the second stage, the mixing ratios of about 12 ppb at 960 K in early January 2004 are in good agreement with MIPAS.

Winter 2004/2005. NH anomalies during the winter 2004/2005 appear more complex to interpret, as two "streaks" of enhancements are observed, one starting early in December which could be interpreted as due to the normal early winter descent, while the second, deep enhancement coincides with the strong SPE of mid-January, and hence could be interpreted as a fast effect. The latter SPE ranked as number 11 of the last

4 decades (Jackmann et al., 2007). However, the high fluxes for the most energetic protons (>100 Mev), supported by calculation of ionisation rates (Seppalla et al., 2006; Verronen et al., 2005) indicate that the SPE penetrated as deep into the stratosphere as the Halloween event. High carbon monoxide (CO) abundance can be used to infer the descent of lower mesospheric air into the stratosphere, and vortex-averaged MLS observations show two separated peaks in CO at the 1400 K near 15 December and 15 January (Manney et al., 2007). Hence the mid-January enhancement can partly be attributed to the SPE (fast effect), but also occurred in a period of strong mesospheric descent.

Winter 2006/2007. A large SPE event occurred in mid-December 2006, associated to solar flares. The SMR HNO_3 observations are only indicative of a two-stage enhancement.

2.2 Southern Hemisphere

Winter 2002. The descending HNO_3 anomaly appears enhanced in conjunction with the occurrence of a SPE event in mid-July 2002.

Winter 2003. The strongest enhancement occurred in austral winter 2003, and was also studied by Stiller et al. (2005) using MIPAS data. They concluded that it originated from strong descent of mesospheric air enriched in NO_x by enhanced auroral activity, and not from a SPE event. Tanskanen et al. (2005) indeed indicated the high occurrence of magnetic substorms and auroral activity in 2003. Some role for the weak SPE event of late May 2003 in enhancing the mesospheric NO_x cannot be ruled out however.

3 Summary and discussion

The time development of the HNO_3 anomalies involves the interplay of middle atmospheric dynamics and chemistry, and solar-terrestrial coupling. While descent of air from the mesosphere into the polar upper stratosphere provides NO_x for HNO_3 heterogeneous conversion, this amount is highly variable, and strongly influenced by EPP. Exceptional enhancements require a large source of NO_x in the form of a strong SPE or an anomalously high auroral activity. Next, dynamics plays a strong role in channelling the descending chemical anomalies. An enhanced descent well-confined in the strong vortex would be leading to large, NO_x stratospheric enhancements, which are a prerequisite for the HNO_3 build-up. Stratospheric sudden warmings could also act to damp the HNO_3 anomalies by bringing air in sunlit regions, and alter the vertical mixing by gravity waves.

Not only the magnitude but also the seasonal timing of EPP events is important. While short-lived HNO_3 enhancements could be triggered by EPP in summer, the long-lasting, descending enhancements can only develop if started not too close from the winter-to-summer transition.

Inspection of Figs. 2 and 3 (as well as Figs. 2 and 3 in Urban et al., 2008) reveals that, in the northern hemisphere, the descending high-altitude enhancements merge with the main layer when the abundance is still high, as clearly seen during the two strongest episodes in 2002 and 2004. In the SH, on the contrary, the descending layer normally reaches the lower stratosphere when the main layer abundance has already decreased considerably. A further point to note is that, as the high-altitude layer descends, the mixing ratios increase indicating continued production.

The ODIN/SMR HNO_3 observations provide for the first time a multi-year record of polar enhancements at high altitudes, and their downward propagation inside the winter polar vortex. Outstanding enhancements are seen during previously studied EPP or strong mesospheric descent events (such as the Halloween storms in late autumn 2003, or the austral winter 2003), but also during more recent ones. The two-stage HNO_3 development first observed by MIPAS (LP05; OR05) has been confirmed on other cases. It takes the form of a short-lived (about 1 week) layer of enriched HNO_3, the fast effect, extending from typically 35 km upwards into the upper stratosphere-lower mesosphere. It is followed by a slowly-developing, descending layer (the delayed effect), characterised by much higher anomalies, up to 10–15 ppb range in unfiltered data. The ODIN/SMR HNO_3 observations nicely show the merging of the descending layer originating at high altitudes with the main layer near 25 km after the seasonal peak.

The descending low or high anomalies appear somewhat analogous to the tropical "tape-recorder" effect, that describes how low-latitude tracer anomalies imprinted at the tropopause level ascend over years, keeping a memory of their initial composition, and giving rise to layered anomalies in the tropical stratosphere. In this case, it is acting at high latitudes, and in reverse (propagating downwards) fashion, and on a faster (seasonal) scale: HNO_3 anomalies are imprinted near the stratopause, descending to the lower stratosphere over the course of the winter, giving rise to layering. The amplitude of the anomalies also increases with time, i.e. during descent, unlike the tape-recorder effect.

Further modelling studies are needed as a step toward implementing appropriate schemes to represent these processes affecting the stratospheric NO_y budget into global chemical transport models.

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References

Austin, J., Garcia, R. R., Russell III, J. M., et al.: On the atmospheric photochemistry of nitric acid, J. Geophys. Res., 91, 5477–5485, 1986.

Bekki, S., Chipperfield, M. P., Pyle, J. A., Remedios, J. J., Smith, S. E., Grainger, R. G., Lambert, A., Kumer, J. B., and Mergenthaler, J. L.: Coupled aerosol-chemical modeling of UARS HNO_3 and N2O5 measurements in the Arctic upper stratosphere, J. Geophys. Res., 102, 8977–8984, 1997.

Bohringer, H., Fahey, D. W., Fehsenfeld, F. C., and Ferguson, E. E.: The role of ion-molecule reactions in the conversion of N_2O_5 to HNO_3 in the stratosphere, Planet. Space Sci., 31, 185–191, 1983.

Callis, L. and Lambeth, J. D.: NO_y formed by precipitating electron events in 1991 and 1992: descent into the stratosphere as observed by ISAMS, Geophys. Res. Lett., 25, 1875–1878, 1998.

de Zafra, R. and Smyshlaev, S. P.: On the formation of HNO3 in the Antarctic mid to upper stratosphere in winter, J. Geophys. Res., 106, 23 115–23 125, 2001.

Jackman, C., DeLand, M. T., Labow, G. J., et al.: Neutral atmospheric influences of the solar proton events in October-November 2003, J. Geophys. Res., 110, A09S27, doi:10.1029/2004JA010888, 2005.

Jackman, C. H., Marsh, D. R., Vitt, F. M., Garcia, R. R., Fleming, E. L., Labow, G. J., Randall, C. E., López-Puertas, M., and Funke, B.: Short- and medium-term atmospheric effects of very large solar proton events, Atmos. Chem. Phys., 8, 765–785, 2008, http://www.atmos-chem-phys.net/8/765/2008/.

Lopez-Puertas, M., Funke, B., Gil-Lopez, S., et al.: Observation of NO_x enhancement and ozone depletion in the Northern and Southern Hemispheres after the October-November 2003 solar proton events, J. Geophys. Res., 110, A09S43, doi:10.1029/2005JA011050, 2005a.

Lopez-Puertas, M., Funke, B., Gil-Lopez, S., et al.: HNO_3, N_2O_5 and $ClONO_2$ enhancements after the October-November 2003 solar proton events, J. Geophys. Res., 110, A09S44, doi:10.1029/2005JA011051, 2005b.

Lopez-Puertas, M. and the IMK/IAA MIPAS team: The effects of SPEs on stratospheric chemistry: MIPAS measurements and model simulation, 4th MIPAS user meetings, Granada, November 2007.

Manney, G. L., Daffer, W. H., Zawodny, J. M., et al.: Solar occultation satellite data and derived meteorological products: sampling issues and comparisons with AURA MLS, J. Geophys. Res., 112, D24550, doi:10.1029/2007JD008709, 2007.
Natarajan, M., Remsberg, E. E., Deaver, L. E., and Russell III, J. M.: Anomalously high levels of NOx in the polar upper stratosphere during April, 2004: Photochemical consistency of HALOE observation, Geophys. Res. Lett., 31, L15113, doi:10.1029/2004GL020566, 2004.
Orsolini, Y. J., Manney, G. L., Santee, M., and Randall, C. E.: An upper stratospheric layer of enhanced HNO_3 following exceptional solar storms, Geophys. Res. Lett., 32(12), L12S01, doi:10.1029/2004GL021588, 2005.
Randall, C. E., et al.: Stratospheric effects of energetic particle precipitation in 2003–2004, Geophys. Res. Lett., 32, L05802, doi:10.1029/2004GL022003, 2005.
Randall, C. E., et al.: Enhanced NOx in 2006 linked to strong upper stratospheric Arctic vortex, Geophys. Res. Lett., 33, L18811, doi:10.1029/2006GL027160, 2006.
Rohen, G., von Savigny, C., Sinnhuber, M., et al.: Ozone depletion during the solar proton events of October/November 2003 as seen by SCIAMACHY, J. Geophys. Res., 110, A09S39, doi:10.1029/2004JA010984, 2005.
Santee, M., Manney, G. L., Livesey, N. J., and Read, W. G., et al.: Three-dimensional structure and evolution of stratospheric HNO_3 based on UARS Microwave Limb Sounder measurements, J. Geophys. Res., 109, D15306, doi:10.129/2004JD004578, 2004.
Santee, M. L., Lambert, A., Read, W. G., et al.: Validation of the AURA Microwave Limb Sounder HNO3 measurements, J. Geophys. Res., 112, D24S40, doi:10.1029/2007JD008721, 2007.
Seppälä, A., Verronen, P. T., Kyrölä, E., Hassinen, S., Backman, L., Hauchecorne, A., Bertaux, J.-L., and Fussen, D.: Solar proton events of October-November 2003: ozone depletion in the Northern Hemisphere polar winter as seen by GOMOS/Envisat, Geophys. Res. Lett., 31, L19107, doi:10.1029/2004GL021042, 2004.
Seppälä, A., Verronen, P. T., Sofieva, V. F., Tamminen, J., Kyrölä, E., Rodger, C. J., and Cliverd, M. A.: Destruction of the tertiary ozone maximum during a solar proton event, Geophys. Res. Lett., 33, L07804, doi:10.1029/2005GL025571, 2006.
Stiller, G., Tsidu, G. M., von Clarmann, T., et al.: An enhanced HNO_3 second maximum in the Antarctic midwinter upper stratosphere in 2003, J. Geophys. Res., 110, D20303, doi:10.1029/2005JD006011, 2005.
Tanskanen, E. I., Slavin, J. A., Tanskanen, A. J., et al.: Magnetospheric substorms are

strongly modulated by interplanetary high-speed streams, Geophys. Res. Lett., 32, L16104, doi:10.1029/2005GL023318, 2005.
Urban, J., Pommier, M., Murtagh, D. P., Santee, M. L., and Orsolini, Y. J.: Nitric acid in the stratosphere based on Odin observations from 2001 to 2007 – Part 1: Global climatology, Atmos. Chem. Phys. Discuss., 8, 9569–9590, 2008, http://www.atmos-chem-phys-discuss.net/8/9569/2008/.
Von Clarmann, T., Glatthor, N., Hopfner, M., et al.: Experimental evidence of perturbed odd hydrogen and chlorine chemistry after the October 2003 solar proton events, J. Geophys. Res., 110, A09S45, doi:10.1029/2005JA011053, 2005.
Verronen, P. T., Seppälä, A., Cliverd, M. A., Rodger, C. J., Kyrölä, E., Enell, C.-F., Ulich, T., and Turunen, E.: Diurnal variation of ozone depletion during the October-November 2003 solar proton events, J. Geophys. Res., 110, A09S32, doi:10.1029/2004JA010932, 2005.

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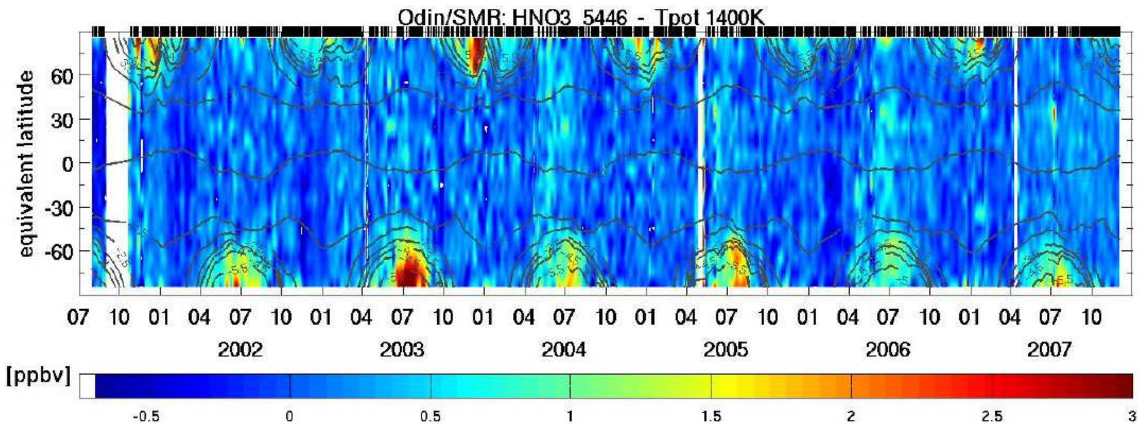

Fig. 1. Time vs. equivalent latitude HNO_3 (ppb) from July 2001 to November 2007, at a potential temperature of 1400 K (near 40 km). Tick marks indicate the beginning of the month.

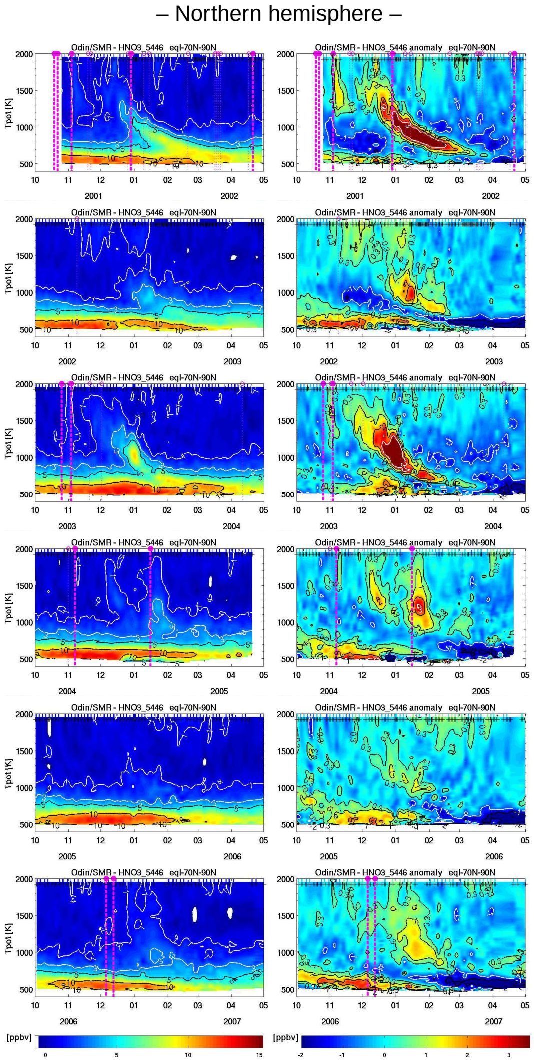

Fig. 2. Time vs. potential temperature evolution of vortex-averaged (equivalent latitudes 70° N–90° N) HNO_3 (ppb) (left column) and deviations from the winter mean (i.e. anomalies, right column), during NH winters 2001/2002 through 2006/2007. X-axis is labelled with months.

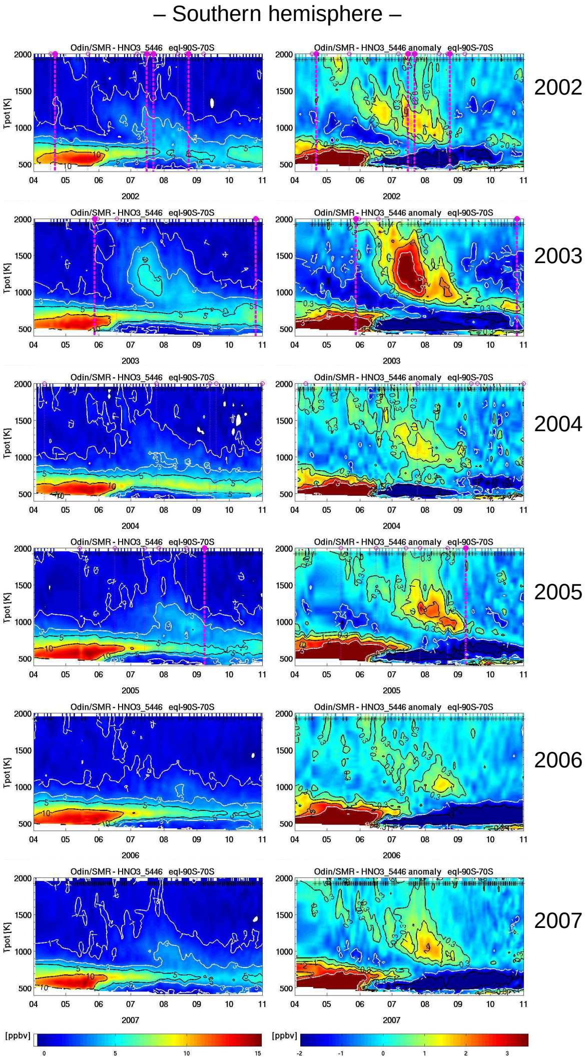

Fig. 3. Same as Fig. 2, for SH (equivalent latitudes 70° S–90° S) winters 2002 through 2007.

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